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TITLE: Diffraction grating for optical application
e.g. for spectrum machine and laser comprises norbornane
based thermoplastic resin with specified surface
roughness

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BASIC-ABSTRACT:

The diffraction grating consists of a thermoplastic resin which has a norbornane structure. The surface of the frame has a linear roughness which are set at parallel intervals in the range of 0.1-1000 units. Chloroform having viscosity in the range of 0.2-1.5 poise is then applied on the surface of the resin. The whole structure is shaped by the compression moulding process.

ADVANTAGE - Performs good optical characteristics,i.e. heat resistance and low water absorption.

TITLE-TERMS: DIFFRACTED GRATING OPTICAL APPLY SPECTRUM MACHINE LASER COMPRISE

NORBORNANE BASED THERMOPLASTIC RESIN SPECIFIED SURFACE ROUGH

DERWENT-CLASS: A89 P81

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H0011*R; S9999

S1434; H0293;

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B9999 B4682

B4568; B9999 B4240*R; B9999 B3407 B3383 B3372; B9999 B3509
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(54) 【発明の名称】 回折格子およびその製造方法

(57) 【要約】

【目的】 光学特性、耐熱性、低吸水性に優れた回折格子、さらに詳しくは分光器、レーザーなどの光学用途に適した回折格子を得る。

【構成】 ノルボルナン骨格を有する熱可塑性樹脂からなり、表面に0.1~1000μmの間隔で平行な直線状の凹凸を有することを特徴とする回折格子ならびに固有粘度(η_{inh})が0.2~1.5dl/g(クロロホルム中、30℃)であるノルボルナン骨格を有する熱可塑性樹脂を射出成形または圧縮射出成形することを特徴とする請求項1の回折格子の製造方法。

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【特許請求の範囲】

【請求項1】ノルボルナン骨格を有する熱可塑性樹脂からなり、表面に0.1〜1000 μ mの間隔で平行な直線状の凹凸を有することを特徴とする回折格子。

【請求項2】固有粘度(η_{inh})が0.2〜1.5 dl/g (クロロホルム中、30℃)であるノルボルナン骨格を有する熱可塑性樹脂を射出成形または圧縮成形することを特徴とする請求項1の回折格子の製造方法。

【請求項3】表面に光線反射率50%以上の金属光沢を持つ金属または金属酸化物の薄膜を蒸着したことを特徴とする請求項1の回折格子。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、光学特性、耐熱性、低吸水性に優れた回折格子に関し、さらに詳しくは分光器、レーザーなどの光学用途に適した回折格子に関する。

【0002】

【従来の技術】従来、回折格子は、透過型ではガラス板の表面に平行にキズをつけたり、ガラス板の表面にレジストを塗布し、これに光学的に凹凸パターンを記入したり、レジストに記入されたパターンを用いガラスをエッチングした後レジストを除去したものが表面で滑性、耐熱性、低吸水性、透明性などの光学特性を生かして使用されているが製作工程が煩雑であり、高価であり、重く組立て時に割れたり、最終商品として使用する場合に衝撃によって割れる欠点を有していた。また、従来回折格子は、反射型では金属光沢のある鏡面にした金属表面に針状のもので機械的に平行なキズをつけたり、レジストに記入されたパターンを用い金属面をエッチングした後レジストを除去したものが表面で滑性、耐熱性、低吸水性、高反射性などの光学特性を生かして利用されているが、製作工程が煩雑であり、高価になり、重いという欠点を有していた。そこで透明な熱可塑性樹脂を回折格子とすることが提案されているが、例えばポリメチルメタクリレートでは、吸水による変形や屈折率の変化が生じ、ポリカーボネートでは金型の形状の転写性に欠けるので表面に凹凸をつけにくく、成形時の残留歪や成形品クランプ時の歪により後屈折が発生するなどの問題があった。

【0003】

【課題を解決しようとする課題】本発明は、これらの問題を一挙に解決し、光学特性、耐熱性、低吸水性に優れた回折格子を提供するものである。

【0004】

【課題を解決するための手段】本発明は、ノルボルナン骨格を有する熱可塑性樹脂からなり、表面に0.1〜1000 μ mの間隔で平行な直線状の凹凸を有することを特徴とする回折格子、さらに必要に応じて表面に光線反射率50%以上の金属光沢を持つ金属または金属酸化物

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の薄膜を蒸着した請求項1の回折格子および固有粘度(η_{inh})が0.2〜1.5 dl/g (クロロホルム中、30℃)であるノルボルナン骨格を有する熱可塑性樹脂を射出成形または圧縮成形することを特徴とする請求項1の回折格子の製造方法を提供するものである。本発明に用いられる熱可塑性樹脂は、その繰り返し単位中にノルボルナン骨格を有するものである。例えば、この熱可塑性樹脂としては、一般式(1)〜(1V)で表されるノルボルナン骨格を含むものである。

【0005】

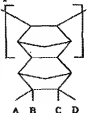
【化1】



(1)

【0006】

【化2】



(1 I)

【0007】

【化3】



(1 II)

【0008】

【化4】



(1 V)

【0009】(式中、A、B、CおよびDは、水素原子または1価の有機基を示す。)

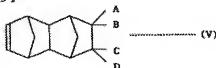
本発明で使用されるノルボルナン骨格を有する熱可塑性樹脂は、充分な強度を得るために、その重量平均分子量は5,000〜100万、好ましくは8,000〜20万である。

【0010】本発明において使用することのできるノルボルナン骨格を有する熱可塑性樹脂としては、例えば特

開昭60-168708号公報、特開昭62-252406号公報、特開昭62-252407号公報、特開平2-133413号公報、特開昭63-145324号公報、特開昭63-264626号公報、特開平1-240517号公報、特開昭57-8815号公報などに記載されている樹脂などを挙げることができる。この熱可塑性樹脂の具体例としては、下記一般式(V)で表される少なくとも1種のテトラシクロドセセン誘導体または該テトラシクロドセセン誘導体と共重合可能な不飽和環状化合物とをメタセシス重合して得られる重合体を水添添加して得られる水添重合体を挙げることができる。

【0011】

【化5】



【0012】(式中、A~Dは、前記に同じ。)

前記一般式(V)で表されるテトラシクロドセセン誘導体において、A、B、CおよびDのうちに極性基を含むことが、密着性、耐熱性の点から好ましい。さらに、この極性基が $-(CH_2)_nCOOR^1$ (ここで、 R^1 は炭素数1~20の炭化水素基、 n は0~10の整数を示す)で表される基であることが、得られる水添重合体が高いガラス転移温度を有するものとなるので好ましい。特に、この $-(CH_2)_nCOOR^1$ で表される極性置換基は、一般式(V)のテトラシクロドセセン誘導体の1分子あたりに1個含有されることが、吸水性を低下させる点から好ましい。前記一般式において、 R^1 は炭素数1~20の炭化水素基であるが、炭素数が多くなると得られる水添重合体の吸湿性が小さくなる点で好ましいが、得られる水添重合体のガラス転移温度とのバランスの点から、炭素数1~4の鎖状アルキル基または炭素数5以上の(多)環状アルキル基であることが好ましく、特にメチル基、エチル基、シクロヘキシル基であることが好ましい。

【0013】さらに、 $-(CH_2)_nCOOR^1$ で表される基が結合した炭素原子に、同時に炭素数1~10の炭化水素基が置換基として結合されている一般式(V)のテトラシクロドセセン誘導体は、吸湿性を低下させるので好ましい。特に、この置換基がメチル基またはエチル基である一般式(V)のテトラシクロドセセン誘導体は、その合成が容易な点で好ましい。具体的には、8-メチル-8-メトキシシクロドセシレン誘導体(4、

4、0、12⁵ 17¹⁰)ドデカ-8-エンが好ましい。

これらのテトラシクロドセセン誘導体、あるいはこれと共重合可能な不飽和環状化合物の混合物は、例えば特開平4-77520号公報第4頁右欄第12行~第6頁右欄第6行に記載された方法によって、メタセシス重

合、水添添加され、本発明に使用される熱可塑性樹脂とすることができる。

【0014】本発明において、ノルボルナン骨格を有する熱可塑性樹脂は、クロロホルム中、30℃で測定される固有粘度(η_{inh})が、0.2~1.5dl/g、好ましくは0.3~1.0dl/gである。固有粘度(η_{inh})が0.2dl/g未満では、機械的特性に劣り、耐衝撃性が低下し、一方1.5dl/gを超えると、加工性が劣り、また射出成形性が劣る。また、水添重合体の水添添加率は、60MHz、 ^1H-NMR で測定した値が50%以上、好ましくは90%以上、さらに好ましくは98%以上である。水添添加率が高いほど、熱や光に対する安定性が優れた回折格子が得られる。なお、本発明のノルボルナン骨格を有する熱可塑性樹脂として使用される水添重合体は、回折格子成形におけるシルバーストリークなどの不良発生防止の面から該水添重合体中に含まれるゲル含有量が重量%以下であることが好ましく、さらに1重量%以下であることが特に好ましい。

【0015】本発明に使用されるノルボルナン骨格を有する熱可塑性樹脂には、必要に応じてその耐候性および耐光性を向上させるために、例えばベンゾトリアゾール系、ベンゾフェノン系、サリチル酸系、シアノアクリレート系などの紫外線吸収剤をはじめ、ヒンダードアミン系、ニッケル錯塩系、ベンゾエート系などの紫外線安定剤を配合することができる。また、酸化防止剤、黄変防止剤、内部離型剤、帯電防止剤、レベリング剤などのいかなる添加剤を加えることも可能である。これらの添加剤の添加方法としては、ポリマーの製造工程中でベレット化する前の溶液にこれらの添加剤を溶解し脱泡してもよいし、リボンブレンダー、タンブラーブレンダー、ヘンシェルミキサーなどで脱泡されたベレットまたは粉体またはクラム状の樹脂とこれら添加剤を混合してもよいし、一軸または多軸の押出機やユーズー、バンドリミキサー、ロールを用いて樹脂を溶融させた中にこれら添加剤を混練してもよい。本発明の回折格子は、ノルボルナン骨格を有する熱可塑性樹脂を射出成形もしくは圧縮成形することにより形成することができる。

【0016】本発明の回折格子は、その表面に0.1~1000 μm 、好ましくは0.4~100 μm の間隔で平行な直線状の凹凸を有するものであるが、この凹凸は前記の金型の表面に所望する間隔で直線状の凹凸を形成しておき、これを成形時にノルボルナン骨格を有する熱可塑性樹脂の表面に転写することにより形成することができる。また、この凹凸の深さは通常0.01~10 μm 、好ましくは0.1~1 μm である。本発明において、金型表面に所定の凹凸をつける方法としては、平滑に鏡面仕上げされた面に、鋭利な刃物係物で傷をつける方法、フォトレジストを塗布し、電子ビームまたは放射線により回折パターンを焼き付け、フォトレジストをパターに従い除去した後、プラズマなどによるドライエッ

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チングや薬品を用いた化学エッチングにより金属表面に凹凸を形成する方法などが挙げられる。

【0017】本発明において射出成形または圧縮成形時の樹脂温度は、通常、230～360℃、好ましくは260～340℃である。樹脂温度が低いと流動性が悪化し、成形品に歪が生じ、360℃を超えると樹脂の分解によりシルバーストリークが生じたり、黄色に着色したり、回折格子のパターンの転写不良がおきやすい。また、圧縮成形時の金型加熱温度は、通常、0～360℃、好ましくは160～340℃であり、冷却時の温度は-40～200℃、好ましくは0～150℃である。射出成形では、金型温度は使用する熱可塑性樹脂のガラス転移温度よりも低い温度で設定することが一般的である。得られる平板の歪を小さくするためにはガラス転移温度に近い温度に設定することが好ましいが、冷却時間を要し、サイクルタイムが長くなったり、割離が生じたりする。金型温度を低い温度に設定すると歪が大きくなるが、サイクルタイムは短くなる。従って好ましい金型温度は、樹脂のガラス転移温度より10℃から80℃低い温度であり、さらに好ましくは20℃から60℃低い温度である。また、樹脂温度は、極めて高い温度であるのでシリンダー内の滞留時間は60分以下になるよう成型機あるいはサイクルタイムを設定することが好ましい。

【0018】本発明の回折格子は、大きさは5mm角あるいはそれ以下の小さなものから、60cm角あるいはそれ以上の大きなものに適用することができる。本発明の回折格子の表面精度は金型の表面精度に依存し、各用途の要求に従って決められる。通常、光学用途では凹凸が10μm以下のものが一般的に使用される。本発明の回折格子の厚さは、製品強度や製品の組立時の作業性や、製品デザイン上で決められる。特にA4サイズ以上の大きさでは、たわみが生じ易くたわみを実用上の品質で抑制するためには、厚さ10μm以上、好ましくは0.05～5mmである。本発明の回折格子の具体的な用途としては、光ディスク用レーザー光学系に用いられる回折格子や増倍長レーザー光線を非線形光学素子を用いて増倍波長光を作り基本波と分離するときに用いる波長分別用の回折格子などに好適に用いることができる。光ディスク用レーザー光学系での利用例としては、MD

等でトラッキング用ビームをメインビームから一定の角度の方向に発生するビームスプリッターとしての利用があげられる。

【0019】

【実施例】以下、実施例を挙げて本発明をさらに具体的に説明するが、本発明は以下の実施例に限定されるものではない。なお、実施例中、部および％は、特に断らない限り重量基準である。なお、実施例中の各種の測定は、次のとおりである。

固有粘度 (η_{inh})

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溶媒にクロロホルムを使用し、0.5g/dlの重合体濃度で30℃の条件下、ウベロー粘度計にて測定した。

水添率

水添単独重合体の場合には、60MHzでスーパーバースイリットH-NMRを測定した。

ガラス転移温度

走査熱量計 (DSC) により、チャッ素雰囲気下において、10℃/分の昇温速度で測定した。

【0020】参考例1

8-メチル-8-メトキシカルボニルテトラシクロ [4.4.0.1^{2,5}.17¹⁶]ドデカ-3-エン10g、1,2-ジメトキシエタン60g、シクロヘキサン240g、1-ヘキセン9g、およびジエチルアルミニウムクロライド0.96mol/lのトルエン溶液3.4mlを、内容積1リットルのオートクレーブに加えた。一方、別のフラスコに、六塩化タングステンの0.05mol/lの1,2-ジメトキシエタン溶液20mlとパラアルデヒドの0.1mol/lの1,2-ジメトキシエタン溶液10mlを混合した。この混合溶液4.9mlを、前記オートクレーブ中の混合物に添加した。密栓後、混合物を80℃で2.5時間攪拌を行った。得られた重合体溶液に、1,2-ジメトキシエタンとシクロヘキサンの2/8 (重量比)の混合溶液を加えて重合体/溶媒が1/10 (重量比)にしたのち、トリエタノールアミン20gを加えて10分間攪拌した。この重合溶液に、メタノール500gを加えて30分間攪拌して静置した。2層に分層した上層を除き、再びメタノールを加えて攪拌、静置後、上層を除いた。同様の操作をさらに2回行い、得られた下層をシクロヘキサン、1,2-ジメトキシエタンで適宜希釈し、重合体濃度が10%のシクロヘキサン-1,2-ジメトキシエタン溶液を得た。この溶液に20gのパラジウム/シリカマグネシア (日揮化学 (株)製、パラジウム量=5%)を加えて、オートクレーブ中で水素圧40kg/cm²として165℃で4時間反応させたのち、水添触媒をろ過によって取り除き、水添重合体溶液を得た。また、この水添重合体溶液に、酸化防止剤であるベンタエリスリチル-テトラキス (3- (3,5-ジ-tert-ブチル-4-ヒドロキシフェニル)プロピオネート)を、水添重合体に対して0.1%加えてから、280℃で減圧下で脱溶媒を行った。次いで、溶融した樹脂を、チャッ素雰囲気下で押し出し機によりペレット化し、固有粘度0.48dl/g (30℃、クロロホルム中)、水添率99.5%、ガラス転移温度168℃の熱可塑性樹脂Aを得た。

【0021】実施例1

参考例1で得られた熱可塑性樹脂Aを用いて市販の射出成形機に鏡面仕上げの金型を取付け、樹脂温度320℃、金型温度130℃、冷却時間20秒で、10cm×10cm、厚み1mmの回折格子を成形した。ここで金

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the diffraction grating which was suitable for optical applications, such as a spectroscope and laser, in more detail about the diffraction grating excellent in an optical property, heat resistance, and low water absorption property.

[0002]

[Description of the Prior Art] Conventionally, a diffraction grating gives a crack in parallel on the surface of a glass plate in a transmission type, or. Apply resist on the surface of a glass plate, and enter an uneven pattern in this optically, or, What removed resist after etching glass using the pattern as which resist was filled in The slippage in the surface, Although used taking advantage of optical properties, such as heat resistance, low moisture absorption, and transparency, when a manufacturing process was complicated, and broke at an expensive price and heavily at the time of an assembly or used it as an end product, it had a fault which breaks by a shock. A concave grating is conventionally needlelike to the surface of metal made into the mirror plane which has metallic luster in a reflection type, and give a parallel crack mechanically, or, After etching a metal surface using the pattern as which resist was filled in, what removed resist was used taking advantage of optical properties, such as surface smoothness, heat resistance, low moisture absorption, and high reflexivity, but a manufacturing process is complicated, and it became expensive, and had the fault that it was heavy. Then, although using transparent thermoplastics as a concave grating is proposed, For example, at polymethylmethacrylate, by polycarbonate, modification by water absorption and change of the refractive index arose, and since the ***** of the shape of a metallic mold was missing, it was hard to give unevenness to the surface, and there was a problem of a double reflex occurring by the residual strain at the time of shaping or distortion at the time of a mold-goods clamp.

[0003]

[Problem(s) to be Solved by the Invention] This invention solves these problems at once, and provides the diffraction grating excellent in an optical property, heat resistance, and low water absorption property.

[0004]

[Means for Solving the Problem] A diffraction grating this invention's consisting of thermoplastics which has a norbornane framework, and having linear shape unevenness parallel to the surface at intervals of 0.1-1000 micrometers, A diffraction grating and intrinsic viscosity (η_{inh}) of claim 1 which vapor-deposited a thin film of metal or a metallic oxide which furthermore has metallic luster of not less than 50% of ray reflectivity in the surface if needed are 0.2 - 1.5 dl/g (among chloroform). A manufacturing method of a diffraction grating of claim 1 characterized for thermoplastics which has a norbornane framework which is 30 ** by injection molding or carrying out compression molding is provided. Thermoplastics used for this invention has a norbornane framework in the repeating unit. For example, as this thermoplastics, a norbornane framework expressed with general formula (I) - (IV) is included.

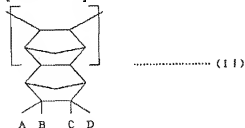
[0005]

[Formula 1]



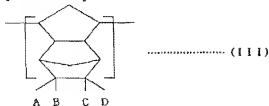
[0006]

[Formula 2]



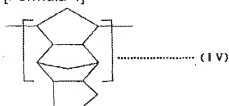
[0007]

[Formula 3]



[0008]

[Formula 4]

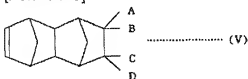


[0009](A, B, C, and D show a hydrogen atom or a univalent organic group among a formula.) in order that the thermoplastics which has a norbornane framework used by this invention may obtain sufficient intensity -- the weight average molecular weight -- 5,000-1 million -- it is 8,000-200,000 preferably.

[0010]As thermoplastics which has a norbornane framework which can be used in this invention, For example, JP,60-168708,A, JP,62-252406,A, The resin etc. which are indicated to JP,62-252407,A, JP,2-133413,A, JP,63-145324,A, JP,63-264626,A, JP,1-240517,A, JP,57-8815,B, etc. can be mentioned. As an example of this thermoplastics, The hydropolymerization object acquired by hydrogenating the polymer produced by carrying out metathesis polymerization of at least one sort of tetracyclo dodecen derivatives or this tetracyclo dodecen derivative expressed with following general formula (V), and the copolymerizable unsaturation ring compound can be mentioned.

[0011]

[Formula 5]



[0012](A-D is the same as the above among a formula.)

In the tetracyclo dodecen derivative expressed with said general formula (V), it is preferred from adhesion and a heat-resistant point that a polar group is included in the inside of A, B, C, and D. Since the hydropolymerization object acquired becomes what has a high glass transition temperature, it is preferred that this polar group is a basis expressed with $-(CH_2)_n$

$COOR^1$ (here, R^1 shows the integer of 0-10, as for the hydrocarbon group of the carbon numbers 1-20 and n). Especially the polar substituent expressed with this $-(CH_2)_n COOR^1$ has a preferred thing of one tetracyclo dodecen derivative per molecule of general formula (V) to contain from the point of reducing absorptivity. In said general formula, although R^1 is a

hydrocarbon group of the carbon numbers 1-20, in that the hygroscopicity of the hydropolymerization object acquired, so that a carbon number increases becomes small, although it is desirable, it is preferred that they are a chain alkyl group of the point of balance with the glass transition temperature of the hydropolymerization object acquired to the carbon numbers 1-4 or a with a carbon numbers of five or more annular (many) alkyl group, and it is preferred that it is especially a methyl group, an ethyl group, and a cyclohexyl group.

[0013] Since a tetracyclo dodecen derivative of general formula (V) in which a hydrocarbon group of the carbon numbers 1-10 is simultaneously combined with a carbon atom which a basis expressed with $-(CH_2)_n COOR^1$ combined as a substituent reduces hygroscopicity, it is preferred. That composition of especially a tetracyclo dodecen derivative of general formula (V) in which this substituent is a methyl group or an ethyl group is preferred at an easy point. Specifically, it is 8-methyl-8-carbomethoxy tetracyclo. $[4.4.0.1^{2,5}1^{7,10}]$ Dodec-8-ene is preferred. A mixture of these tetracyclo dodecen derivatives, or this and a copolymerizable unsaturation ring compound, For example, by a method indicated to the JP,4-77520,A 12th line on the upper right-hand section in page 4 - the 6th line on the lower right-hand section in page 6, it can be considered as metathesis polymerization and thermoplastics which hydrogenation is carried out and is used for this invention.

[0014] In this invention, intrinsic viscosity (η_{inh}) by which thermoplastics which has a norbornane framework is measured at 30 °C among chloroform is 0.3 - 1.0 dl/g preferably 0.2 to 1.5 dl/g. When intrinsic viscosity (η_{inh}) is inferior to a mechanical property in less than 0.2 dl/g, shock resistance falls and 1.5 dl/g is exceeded on the other hand, processability is inferior and injection-molding nature is inferior. A value which measured a hydrogenation rate of a hydropolymerization object by 60 MHz and 1H -NMR is not less than 98% still more preferably not less than 90% preferably not less than 50%. A diffraction grating excellent in stability to heat or light is obtained, so that a hydrogenation rate is high. A hydropolymerization object used as thermoplastics which has a norbornane framework of this invention, It is preferred that gel content contained in this hydropolymerization inside of the body from a field of poor occurrence prevention, such as a silver streak in diffraction grating shaping, is 5 or less % of the weight, and it is preferred that it is especially 1 more or less % of the weight.

[0015] In thermoplastics which has a norbornane framework used for this invention. In order to raise the weatherability and lightfastness if needed, for example A benzotriazol system, UV stabilizer including ultraviolet ray absorbents, such as a benzophenone series, a salicylic acid system, and a cyanoacrylate system, such as a hindered amine system, a nickel complex salt system, and a benzoate system, can be blended. an antioxidant and yellowing - it is also possible to add what is called additive agents, such as an inhibitor, an internal release agent, a spray for preventing static electricity, and a leveling agent. As the addition method of these

additive agents, dissolve these additive agents in a solution before pelletizing in a manufacturing process of polymer, may de** and, May mix a pellet de**(ed) with a ribbon blender, a tumbler blender, a Henschel mixer, etc., a granular material, or crumb-like resin and these additive agents, and, These additive agents may be kneaded to inside which carried out melting of the resin using an extrusion machine of one axis or a multiple spindle, a kneader and a van dolly mixer, and a roll. The diffraction grating of this invention can fabricate thermoplastics which has a norbornane framework injection molding or by carrying out compression molding.

[0016]Although a diffraction grating of this invention has 0.1-1000 micrometers and linear shape desirable unevenness parallel at intervals of 0.4-100 micrometers on the surface, This unevenness forms linear shape unevenness at an interval for which it asks on the surface of the aforementioned metallic mold, and can form it by transferring this on the surface of thermoplastics which has a norbornane framework at the time of shaping. 0.01-10 micrometers of depth of this unevenness are usually 0.1-1 micrometer preferably. In this invention, as a method of giving predetermined unevenness to the metallic mold surface, A method and photoresist which give a crack to a field by which mirror finish was carried out smoothly by a sharp edged tool Mr. thing are applied, After printing a diffraction pattern with an electron beam or radiation and removing photoresist according to a putter, a method of forming unevenness in a surface of metal by chemical etching using dry etching and medicine by plasma etc., etc. are mentioned.

[0017]In this invention, 230-360 ** of resin temperature at the time of injection molding or compression molding is usually 260-340 ** preferably. If resin temperature is low, mobility will get worse, distortion arises in mold goods, if it exceeds 360 **, a silver streak will arise by disassembly of resin, or it is colored yellow, or is easy to set inferior transfer of a pattern of a diffraction grating. moreover -- 0-360 ** of metallic mold cooking temperature at the time of compression molding is usually 160-340 ** preferably -- temperature at the time of cooling -40-200 ** is 0-150 ** preferably. As for a die temperature, in injection molding, it is common to set up at a temperature lower than glass transition temperature of thermoplastics to be used. In order to make small monotonous distortion obtained, it is preferred to set it as temperature near glass transition temperature, but cool time is required, cycle time becomes long or exfoliation arises. If a die temperature is set as a low temperature, distortion will become large, but cycle time becomes short. Therefore, a desirable die temperature is a temperature lower 80 ** than glass transition temperature of resin from 10 **, and is a still more desirable temperature low 60 ** from 20 **. As for holding time in a cylinder, since resin temperature is a very high temperature, it is preferred to set up a briquetting machine or cycle time become in 60 or less minutes.

[0018]The diffraction grating of this invention can apply a size to a 60-cm angle or a big thing

beyond it from 5 mm squares or a small thing not more than it. Surface accuracy of a diffraction grating of this invention is decided according to a demand of each use depending on surface accuracy of a metallic mold. Usually, in an optical application, a thing of 10 micrometers or less is generally used for unevenness. Thickness of a diffraction grating of this invention is decided on product strength, workability at the time of an assembly of a product, and a product design. In order to control a deflection in practical quality with a size more than A4 size especially that it is easy to produce a deflection, it is 0.05-5 mm preferably not less than 10 micrometers in thickness. As a concrete use of a concave grating of this invention, a concave grating and a short wavelength laser beam line which are used for laser optical systems for optical discs can be used conveniently for a concave grating for wavelength judgment etc. which are used when making multiplying wavelength light using a nonlinear optical element and separating from a fundamental wave. As an example of use in laser optical systems for optical discs, use as a beam splitter which generates a beam for tracking in the fixed angle direction from a main beam is raised with MD etc.

[0019]

[Example] Although an example is given and this invention is explained still more concretely hereafter, this invention is not limited to the following examples. Among an example, a part and especially % are weight references, unless it refuses. Various kinds of measurement in an example is as follows.

Chloroform was used for the intrinsic viscosity (η_{inh}) solvent, and it measured by the ubellohde's viscosimeter under a 30 ** condition with the polymer concentration of 0.5 g/dl. In the case of the hydrogenation rate hydrogenation homopolymer, sault pass IRIPUTO H-NMR was measured at 60 MHz.

With the glass-transition-temperature scanning calorimeter (DSC), it measured with 10 ** the heating rate for /under nitrogen atmosphere.

[0020] Reference example 18-methyl-8-carbomethoxy tetracyclo [4.4.0.1^{2,5}.1^{7,10}] 100 g of dodec-3-ene, 60 g of 1,2-dimethoxyethane, the cyclohexane 240g, 9 g of 1-hexenes, and 3.4 ml of toluene solutions (diethylaluminum chloride 0.96mol/l.) were added to autoclave with a content volume of 1 l. On the other hand, 20 ml of 0.05 mol/l. 1,2-dimethoxyethane solutions of tungsten hexachloride, and 1 [0.1 mol/l.] of a paraldehyde and 10 ml of 2-dimethoxyethane solutions were mixed in another flask. 4.9 ml of this mixed solution was added into the mixture in said autoclave. After sealing, the mixture was heated at 80 ** and stirring was performed for 2.5 hours. After it added two eighths of the mixed solvents (weight ratio) of 1,2-dimethoxyethane and cyclohexane to the obtained polymer solution and the polymer/solvent made it it at 1/10 (weight ratio), 20 g of triethanolamine was added and it stirred for 10 minutes. It added, and the methanol 500g was stirred to this polymerization solution for 30 minutes, and was settled on it. Except for the upper layer divided into two-layer, methanol was added again

and the upper layer was removed after stirring and settlement. The lower layer obtained by performing same operation twice [further] was suitably diluted with cyclohexane and 1,2-dimethoxyethane, and the cyclohexane- 1 and 2-dimethoxyethane solution whose polymer concentration is 10% were obtained. They are 20 g of palladium/silica magnesia to this solution. After adding [the product made from JGC Chemicals, and amount =of palladium5%] and making it react at 165 °C as hydrogen pressure 40 kg/cm² in autoclave for 4 hours, the hydrogenation catalyst was removed by filtration and the hydropolymerization object solution was obtained. Pentaerythritol tetrakis which is an antioxidant at this hydropolymerization object solution After adding [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] 0.1% to the hydropolymerization object, it deliquored under decompression at 280 °C. Subsequently, the fused resin was pelletized with the extruder under nitrogen atmosphere, and the with intrinsic viscosity 0.48 dl/g (inside of 30 °C and chloroform), the hydrogenation rate of 99.5%, and a glass transition temperature of 168 °C thermoplastics A was obtained.

[0021]The metallic mold of mirror finish was attached to the commercial injection molding machine using the thermoplastics A obtained by the example 1 reference example 1, and 10 cm x 10 cm, and a 1-mm-thick diffraction grating were fabricated in resin temperature [of 320 °C], die-temperature [of 130 °C], and cool time 20 seconds. Beforehand, 6.23 micrometers of intervals were formed in the scribing barricade, and 100 parallel straight lines were formed in the metallic mold surface in a depth of 0.5 micrometer here. Extraction from the metallic mold of the molded product after shaping was projected by the pin, and two projections for ejection were set as the monotonous end. The crack by a silver streak, HAKURI, etc. was not found in the obtained diffraction grating. 92%, less than 1%, as for the variation in thickness, vertical incidence of the double reflex was [light transmittance of the mirror surface part of the obtained diffraction grating] also a small thing of 20 nm or less also in slanting incidence, and unevenness was 10 micrometers or less and was a level possible as an optical application. When 623-nm laser beams were entered at right angles to the diffraction grating part of the center section of the diffraction grating, since the spot up to the 5th order was clearly accepted at intervals of about 10 cm at the place whose emitted light is 1 m, it checked functioning as a diffraction grating.

[0022]The diffraction grating was fabricated like Example 1 except having used polycarbonate (made in Teijin Chemicals, L1225) instead of the thermoplastics A obtained by the comparative example 1 reference example 1. 87%, 1.5%, the variation in thickness was 300 nm in 100 nm and 45-degree oblique incidence, and the light transmission of the double reflex of the mirror surface part of the obtained diffraction grating was unsuitable [variation] at vertical incidence as an optical application. When 623-nm laser beams were entered still at right angles to the diffraction grating part of a diffraction grating center section, at intervals of about 10 cm, the spot up to the 2nd order had faded, and its transfer of the diffraction grating pattern of a

metallic mold was bad to the place whose emitted light is 1 m, and it was not functioning enough as a diffraction grating at it.

[0023]Reference example 28-ethyl-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] 100 g of dodec-3-ene, 60 g of 1,2-dimethoxyethane, the cyclohexane 240g, 9 g of 1-hexenes, and 3.4 ml of toluene solutions (diethylaluminum chloride 0.96mol/l.) were added to autoclave with a content volume of 1 l. On the other hand, 20 ml of 0.05 mol/l. 1,2-dimethoxyethane solutions of tungsten hexachloride, and 1 [0.1 mol/l.] of a paraldehyde and 10 ml of 2-dimethoxyethane solutions were mixed in another flask. 4.9 ml of this mixed solution was added into the mixture in said autoclave. After sealing, the mixture was heated at 80 °C and stirring was performed for 2.5 hours. After it added two eighths of the mixed solvents (weight ratio) of 1,2-dimethoxyethane and cyclohexane to the obtained polymer solution and the polymer/solvent made it at 1/10 (weight ratio), 20 g of triethanolamine was added and it stirred for 10 minutes. It added, and the methanol 500g was stirred to this polymerization solution for 30 minutes, and was settled on it. Except for the upper layer divided into two-layer, methanol was added again and the upper layer was removed after stirring and settlement. The lower layer obtained by performing same operation twice [further] was suitably diluted with cyclohexane and 1,2-dimethoxyethane, and the cyclohexane- 1 and 2-dimethoxyethane solution whose polymer concentration is 10% were obtained. They are 20 g of palladium/silica magnesia to this solution. After adding [the product made from JGC Chemicals, and amount =of palladium5%] and making it react at 165 °C as hydrogen pressure 40 kg/cm² in autoclave for 4 hours, the hydrogenation catalyst was removed by filtration and the hydropolymerization object solution was obtained. Pentaerythrityl tetrakis which is an antioxidant at this hydropolymerization object solution After adding [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] 0.1% to the hydropolymerization object, it deliquored under decompression at 280 °C. Subsequently, the fused resin was pelletized with the extruder under nitrogen atmosphere, and the with intrinsic viscosity 0.48 dl/g (inside of 30 °C and chloroform), the hydrogenation rate of 99.5%, and a glass transition temperature of 138 °C thermoplastics B was obtained.

[0024]The metallic mold of mirror finish was attached to the commercial injection molding machine using the thermoplastics B obtained by the example 2 reference example 2, and 10 cm x 10 cm, and a 1-mm-thick diffraction grating were fabricated in resin temperature [of 290 °C], die-temperature [of 100 °C], and cool time 20 seconds. Beforehand, 3.12 micrometers of intervals were formed in the scribing barricade, and 100 parallel straight lines were formed in the metallic mold surface in a depth of 0.3 micrometer here. Extraction from the metallic mold of the molded product after shaping was projected by the pin, and two projections for ejection were set as the monotonous end. The obtained mold goods vapor-deposited the aluminum reflection film on the surface, and used it as the diffraction grating which attaches HOGOKOTO and has receipts and payments of light from the resin side on it. The crack by a silver streak,

HAKURI, etc. was not accepted. 92%, less than 1%, as for the variation in thickness, vertical incidence of the double reflex was [rate of a light reflex of the mirror surface part of the obtained diffraction grating] also a small thing of 20 nm or less also in slanting incidence, and unevenness was 10 micrometers or less and was a level possible as an optical application. When 623-nm laser beams were entered at right angles to the diffraction grating part of the center section of the diffraction grating, since the spot up to the 5th order was clearly accepted at intervals of about 20 cm at the place whose emitted light is 1 m, it checked functioning as a diffraction grating.

[0025]

[Effect of the Invention] Since the diffraction grating which consists of thermoplastics which has a norbornane framework of this invention is fabricated with injection molding or compression molding, the unevenness according to the surface accuracy of the metallic mold is transferred good, there is no coloring, and it has the function outstanding as a diffraction grating. It is also possible for the shape of mold goods to be changeable with a metallic mold, and for it not to be necessary to cut and to unite shape after shaping, and to build puncturing, the projection for a clasp, etc. with shaping at the time of said.

[Translation done.]